Organics, meteoritic material, mercury, and other elements in high altitude aerosols

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Abstract

Recent in situ measurements of the chemical composition of single aerosol particles at altitudes up to 19 km have revealed a number of surprising features about ambient particles. Upper tropospheric aerosols in the study region often contained more organic material than sulfate. Although stratospheric aerosols are primarily sulfuric acid and water, many also contain meteoritic material. Just above the tropopause, small amounts of mercury were found in over half of the aerosol particles that were analyzed. There was tremendous variety in aerosol composition. One measure of this diversity is that at least 45 elements were detected in aerosol particles at altitudes between 5 and 19 km.

Introduction

Understanding the composition of atmospheric aerosol particles is necessary both to understand their sources and to predict their effects on atmospheric chemistry and climate. Aerosols impact the earth's heat budget both directly by absorbing and scattering sunlight and indirectly by acting as nuclei for cloud droplets. These aerosol effects contribute some of the most important uncertainties associated with global-mean radiative forcing (1). Aerosols also affect gas phase chemistry through the effects of heterogeneous chemistry. In the stratosphere, aerosols have major impacts on polar ozone depletion when they take up nitric acid and water at cold temperatures to form polar

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stratospheric clouds (2). Heterogeneous reactions are known to affect the NO_x budget throughout the lower stratosphere and have been suggested as a way of resolving discrepancies in the NO_x budget of the upper troposphere. Recent changes in various anthropogenic and natural species in the atmosphere could lead to shifts in the number, size, and composition of aerosols and potentially influence atmospheric chemistry. Increased air traffic is of special concern for injecting material that could affect aerosols at high altitudes (3).

It has been known since the 1960's that the stratospheric aerosol layer is mostly sulfate and associated water (4, 5). An early suggestion that many stratospheric aerosols contain meteoritic material (6) was later disputed (7). Besides particles that are primarily sulfuric acid, a few percent of stratospheric particles have widely varying compositions including soot and minerals (8). Aerosols in the upper troposphere are not as well characterized as those in the lower stratosphere. Most modelling studies have assumed that upper tropospheric aerosols are either ammonium sulfate or sulfuric acid.

The development of the measurements described here started with the recognition there were few measurements of volatile or trace species in stratospheric aerosols. Temperatures at 12-19 km altitude are usually less than 225 K, so bringing either filter samples or electron microscope grids back for laboratory analysis at room temperature involves heating the samples by over 75 K. Such heating risks significant changes in composition. Sulfuric acid aerosols also readily take up ammonia and organics from air (9, 10), so any sample handling can affect those species. The measurements described here are also much more sensitive to many trace species than previous techniques used to analyze stratospheric aerosols.

2

Method

Particles were analyzed using a laser ionization mass spectrometer (11, 12). Aerosols are brought into a vacuum system and detected by light scattered as they cross the beam of a continuous laser. The scattered light signal gives a trigger and a rough indication of the size of the particle. An excimer laser (193 nm) is pulsed so the beam hits the particle to desorb and ionize molecules and atoms. These ions are analyzed with a time of flight mass spectrometer to provide a complete mass spectrum from each particle. Laser pulses with no aerosols present produce less than 0.1% of the signal from a typical particle so that the spectra are representative of aerosol species only. For example, the system is sensitive to aerosol nitrate but not gas phase nitric acid. Calibrations with KCl particles and latex spheres indicate a minimum detectable particle size of about 0.2 μm diameter for the flight instrument. Particles larger than 0.2 μm included a majority of the aerosol mass in the upper troposphere and lower stratosphere but usually only a minority of the number of particles (13).

Artifacts are minimized because the particles never touch a surface and because the analysis is complete less than 7 ms after the aerosols enter the inlet into the aircraft, where they are adiabatically heated by an estimated 6 K, and less than 1 ms after the aerosols enter the vacuum chamber. Although this is more than enough time for evaporation or condensation of monolayers of volatile species, mass transfer calculations indicate that there should not be any substantial changes in the bulk composition of aerosols. Spectra of water were observed in cirrus clouds, indicating that at least some of even the most volatile particles survived into the instrument.

The particle analysis by laser mass spectrometry (PALMS) instrument was mounted in the nose of a WB-57F high altitude research airplane. Flights were made from Houston over a latitude range from 10 to 46 degrees north latitude and altitudes up to 19 km. Mass spectra were obtained from

over 28,000 individual particles. By changing the acceleration voltages, the mass spectrometer can transmit either positive or negative ions to the detector. The polarity was changed every few minutes in flight with about 2/3 of the time spent acquiring positive spectra. Except during time spent in cirrus clouds, mass spectra were obtained from well over 90% of valid triggers. Therefore, we can be confident that these data include all of the common types of aerosols larger than 0.2 μm.

A microwave temperature profiler (MTP) on the WB-57F measured the temperature above and below the airplane (14). The position of the tropopause was then derived from the temperature profiles from the WMO definition for the thermal tropopause.

Sulfate and organics

Most of the negative ion spectra of stratospheric aerosols were simple, as shown in Figure 1a. Sulfate was the predominant component. Only a few percent of the aerosols had compositions in which sulfate was not dominant, in agreement with Sheridan et al. (8). In the upper troposphere, many of the negative ion spectra were more complicated (Figure 1b). As in this example, organic peaks were very common in the upper troposphere. Organics and sulfates were usually present in the same particles (internally mixed). Besides the particle types shown in Figure 1, negative ion spectra of mineral particles and soot particles were also observed. These were occasionally present well above the tropopause but were more common in the troposphere.

Figure 2 shows average profiles of the sulfate and organic peaks, expressed as fractions of the total ion current. The tropopause was associated with a distinct change in composition. In the stratosphere, sulfate peaks dominated the negative ion spectra. As in Figure 1a, the remaining negative ions were mostly O⁻ and OH⁻. In the upper troposphere, organic ions were often more

4

abundant than sulfate peaks. Since sulfate makes negative ions such as HSO_4^- very readily, the negative ion spectra are generally more sensitive to sulfate than to organics (10). Therefore, the ion fractions shown are most likely upper limits for the mole fractions of sulfate. Positive ion spectra, which are much more sensitive to organics, demonstrate the presence of a small but definitely non-zero concentration of organics in stratospheric aerosols.

Meteoritic material in stratospheric aerosols

Iron was present in about half of the spectra of stratospheric aerosols, and was often the largest positive ion peak (Figure 3a). The ^{54}Fe and ^{56}Fe isotopes allow us to identify iron with confidence. Peaks such as $H_3SO_4^+$ in the spectra indicate that the iron was present in sulfate aerosols. Since metals make positive ions much more readily than sulfate does, even small molar fractions of metals can be easily observed in the positive ion spectra of stratospheric sulfate aerosols.

These iron-containing spectra in the stratosphere also exhibited magnesium and other elements in quite constant proportions. The $^{24}Mg/^{56}Fe$ and $^{58}Ni/^{56}Fe$ ratios had standard deviations of about 50% of their mean values, which are extremely narrow distributions for laser ionization of aerosols. For comparison, the accuracy with which the peaks could be measured limited the standard deviation of $^{54}Fe/^{56}Fe$ to about 14%. Sodium, aluminum, potassium, calcium, and chromium also were correlated with the iron in stratospheric aerosol particles.

Spectra with large iron peaks were much more common in the stratosphere than in the troposphere (Figure 4). Although more calibrations are required to convert ion fractions to mass fractions, the

shift in Figure 4 is sufficiently large to show that the fractional iron content of aerosols is larger in the stratosphere than in the troposphere. A high altitude source combined with the other elements present in the spectra indicates a meteoritic source for the iron and other metals in the stratospheric aerosols. Figure 5 presents the $^{39}K/^{23}Na$ ratio in particles that contain iron. The stratospheric $^{39}K/^{23}Na$ ratio is quite distinct from the larger and much more variable ratio at lower altitudes. The stratospheric ratio is close to the $^{39}K/^{23}Na$ measured at about 100 km altitude after the 1976 Perseid meteor shower [15]. The larger and more variable tropospheric ratios are consistent with sources such as mineral dust. Iron in stratospheric aerosols was not correlated with the particle size estimated from the scattered light pulse.

Most of the mass of meteors is in particles less than 1 mm in diameter which ablate at altitudes above 75 km [16, 17], providing a source for metal atoms in the upper atmosphere. These atoms eventually recombine to form "smoke" particles estimated to be less than 20 nm in diameter [16]. Although the free atoms, especially Na, are measurable [18], the condensed particles are not easily observed. Presumably, the smoke particles undergo coagulation as the mesospheric air descends followed by the condensation of sulfuric acid in the stratosphere. By the time the material has descended to 40 km, free metal atoms are no longer observable[19]. Meteoritic smoke particles may be very homogeneous in composition [16], and coagulation should further homogenize them. The constancy of the $^{24}Mg/^{56}Fe$ ratio in our mass spectra is consistent with a very homogeneous material.

The influx of meteoritic material into the earth's atmosphere has been estimated as 12 Gg year^{-1} based on meteorite statistics [20] and (40±20) Gg year^{-1} based on the Long Duration Exposure Facility [21]. The majority of this incoming mass is expected to ablate. Models of Na and Fe ions

in the upper atmosphere yield deposition of meteoritic material into the mesosphere of 2 to 4 Gg year[-1] (17, 22).

For comparison to the flux of meteoritic material, a total source of 100 to 160 Gg year[-1] of sulfur from oxidation of OCS and SO_2 appears necessary to maintain the stratospheric aerosol layer (23, 24, 25, 26). When converted to aerosols that are by weight 70% sulfuric acid and 30% water, this represents a source of 440 to 700 Gg year[-1] of condensible material. If we assume similar residence times in the stratosphere for meteoritic material and the condensing sulfuric acid then the ratio of the fluxes gives an estimate of the composition of the stratospheric aerosol layer. An additional uncertainty is introduced because the actual mass available for incorporation into stratospheric aerosols may be different than the incident mass as the oxygen bound into minerals and oxides is released during ablation and then accumulated during later oxidation of iron, silicon, and other elements. Using 4 to 30 Gg year[-1] of ablated meteoritic material, the stratospheric aerosol layer would be expected to be 0.6 - 7% meteoritic material by mass. The upper limit is scarcely credible, as it probably violates constraints posed by electron microscopy of aerosols collected on impactors (8) as well as observations of the volatility of stratospheric aerosols (27).

Mercury

Surprisingly, many high altitude particles contained mercury. As shown in Figure 3c, mercury can be identified unambiguously from its isotopic pattern. Although the example in Figure 3c is from well into the mid-latitude stratosphere, aerosols containing mercury were most common just above the tropopause. Figure 6 shows the vertical distribution of mercury relative to the tropopause. The mercury was distributed as small peaks present in about half of the particles near the tropopause. Over 70% of the spectra during one flight leg near the tropopause south from Houston to 10° N

mercury. Because the mercury peaks were often near the detection limit, an even larger fraction of particles may have contained mercury. In contrast to these results, no mercury was detected in over 2600 positive ion spectra taken with PALMS at a remote continental surface site (Idaho Hill, Colorado) nor was any mercury detected in over 9000 positive ion spectra at a remote marine surface site (Cape Grim, Tasmania).

Mercury and some important mercury compounds are semi-volatile (28). Because its long atmospheric lifetime, condensation onto aerosols is thought to be an important sink for atmospheric mercury even though only about 1% of atmospheric mercury at low altitudes is in aerosols (29).

The strong gradient in aerosol mercury at the tropopause could be due to the conversion of mercury to less volatile forms in the stratosphere. It is not due to simple condensation, as the vapor pressure of mercury at 190 K is about 3×10^{-9} mbar (30), approximately 100 times the partial pressure expected if there were 2 ppt by mass of atomic mercury in the gas phase (29, 31) at the tropopause. Atomic mercury reacts slowly with O_3 (32) to form HgO, which has a low enough vapor pressure to condense at ppt concentrations (28). More work is required to check if the reaction with O_3 can account quantitatively for the gradient of particulate Hg above the tropopause or if other reactions are required. Another possibility for the gradient above the tropopause is that condensed mercury could be present at the tropopause but on aerosol particles too small for PALMS to detect. Very small aerosol particles are especially abundant near the tropical tropopause (33) and coagulate in the lower stratosphere.

The expected concentration of mercury in aerosols above the tropopause can be estimated as 0.1% by mass by comparing 2 ppt by mass of condensible mercury with the approximately 2 ppb by mass of aerosol measured just above the tropopause (13). The Hg ion signal shown in Figure 6 is

more than expected. Mercury has a very high ionization potential (10.4 eV), so that laser ionization mass spectrometers are relatively insensitive to mercury (34, 35). Further calibrations for laser ionization of mercury at 193 nm are needed to better determine the concentration of mercury in aerosols.

Unlike iron, mercury peaks showed a strong positive correlation with amount of light scattered by each particle. This could indicate that larger particles contained relatively more mercury or it could be an artifact of dealing with peaks near the detection limit. Particles that travel through the edges of the laser beams produce smaller than average scattered light pulses and also tend to give spectra with lower signal levels, making it harder to detect trace constituents such as mercury in those particles.

Aerosol diversity

Besides some of the more common types of particles presented in Figures 1 and 3, a wide variety of unusual particles were observed. Of course it is not possible to display all of the unusual particles, but examples are shown in Figure 7. Together with the unusual particles, the presence of meteoritic material, mercury, and organics means that aerosols contain many more elements than those present in just sulfate. Figure 8 shows some approximate frequencies of various elements. The most common mass peaks were sulfate, organics, and NO^+, so that H, C, O, N, and S were found in almost every particle. The elements Na, Mg, Al, K, Ca, Cr, Fe, and Ni were commonly measured with the meteoritic material. Halogens were found in many particles in the upper troposphere (Figure 1b), and also in some stratospheric aerosols. At least 45 elements were found in aerosol particles above 5 km. Of these, perhaps 35 elements were found in the stratosphere.

A few of the rarer elements merit special comments. Boron was observed in about 4% of the spectra and was observed at all altitudes and latitudes. Its sources and aerosol chemistry are not well known. Barium was present in a very high fraction of particles during a few short stretches of flight just below the tropopause, mostly south of Houston. Particles containing rubidium almost always had a much larger potassium peak. Lead was significantly more common than the other heavy metals besides mercury. Bismuth was present in a few particles in the stratosphere, where it is thought to come from volcanic material (36). The rare earths were found in two upper tropospheric spectra that also contained Al, Sr, and Ba.

Discussion

The observation that organics can contribute more mass than sulfate to aerosols in portions of the upper troposphere is significant both for the mass balance of aerosols in the troposphere and for the optical and cloud nucleation properties of aerosols. There are few data on organic aerosols in the free troposphere. Our data are consistent with Novakov et al. (37), who found that organics contributed a majority of the aerosol mass at 2-3 km over the North Atlantic. Organics are likely to be important for the optical properties of upper tropospheric aerosols. Satellite retrievals that treat aerosols only as sulfuric acid or ammonium sulfate may not give adequate results.

These data are among the first observations of ablated meteoritic material after it has condensed to form particles and descended to altitudes of less than about 70 km. Recent work has shown that a large fraction of the descent of air from the mesosphere into the stratosphere is concentrated in the winter polar regions (38). High numbers of aerosols less than 0.1 μm in diameter have been observed in the winter polar stratosphere (39, 40). The data presented here would suggest that meteoritic material is responsible for many of these particles. Although Zhao et al. (41) concluded that there would be large numbers of aerosols in the polar stratosphere with or without meteoritic

10

input, one must ask if the size distribution in the stratosphere is sensitive to the presence of these nuclei. Are there smaller but more numerous particles in the stratosphere because of the input of meteoritic nuclei? Changes in the size distribution affect the surface area and hence the potential for heterogeneous chemistry. Earlier studies (42) used one-dimensional models, which cannot capture the nature of the exchange between the stratosphere and higher altitudes. The concentration of meteoritic material in stratospheric aerosols is too low to significantly change the refractive index, but meteoritic material may be important for optical properties if it absorbs light at certain wavelengths.

These data provide intriguing possibilities for tracking the origins of stratospheric aerosol particles. Besides the winter poles, aerosol particles are also produced in large numbers at the tropical tropopause (33). If there is meteoritic material in the particles formed during descent from high altitudes and mercury in many of the particles formed near the tropopause, then the fractions of aerosols with various compositions could provide direct tests of stratospheric transport. Meteoritic material and mercury were almost always on separate particles, but there were a handful of particles with both. The frequency of such mixed particles might provide a test of the rate of coagulation of aerosols in the stratosphere. The observation of particles which contain neither meteoritic material nor mercury (Figure 3b) leaves open the possibility of a third region of new particle formation in the stratosphere. The chemical composition of aerosols in the stratosphere and troposphere seem to be sufficiently unique so that the exchange of aerosols could be tracked. For example, we observed a few particles with an unequivocal meteoritic and sulfate signal in the troposphere. Further flight data may help answer questions about whether or not stratospheric aerosols can indirectly affect the climate by serving as nuclei for cirrus clouds.

The observation of mercury at altitudes up to 19 km provides a dramatic example of how emissions from the surface can reach remote portions of the atmosphere. It also provides strong support for

11

the estimates of a long lifetime for gaseous mercury in the atmosphere (28).

Finally, the presence of unusual particles could have an importance far beyond their numbers. Both cirrus clouds and polar stratospheric clouds often nucleate on only a fraction of a percent of the available aerosols. Recent research has found that ice nuclei and cirrus crystal residues at 9-11 km altitude have very different compositions than the majority of particles (43, 44). Our data indicate that cloud formation processes have an extremely diverse pool of particles to draw from in finding ice and cloud nuclei. Although unablated meteoritic material is not suitable as nuclei for nitric acid hydrates (45), some of the uncommon particles could conceivably provide freezing nuclei for such stratospheric clouds. If nitric acid hydrates freeze only on a few nuclei, then those particles may grow larger and sediment out to denitrify the lower polar stratosphere.

A number of aspects of the PALMS aircraft data remain to be explored. Some spectra showed chlorine and/or other halogens in the aerosol particles. Soot was also observed in the upper troposphere. More flights within 10° latitude of the equator, where air enters the stratosphere, would help explore how tropospheric aerosols may affect the stratosphere. Future flights comparing mid-latitude tropospheric aerosols in the Northern and Southern hemispheres could explore the reasons why there is more aerosol mass in the Northern Hemisphere upper troposphere (46) and the related question of anthropogenic influences on aerosols on a global scale (50).

Figure 1: Examples of negative ion spectra obtained from single aerosol particles in the (a) stratosphere and (b) the upper troposphere. These spectra were chosen to be typical of the most common spectra observed in each altitude range. The stratospheric particle spectrum also had a peak at $195 = H_2SO_4 \cdot HSO_4^-$. The tropospheric particle spectrum shows organic and sulfate peaks along with halogens. The presence of organic acids and $CH_2(OH)SO_3^-$, which is most likely a fragment of hydroxymethanesulfonic acid (HMSA) (47), may indicate a role of liquid cloud processing of this particular aerosol.

Figure 2: Average profiles of the fractions of ion current in sulfate and organic peaks as a function of potential temperature. Sulfate was approximated as the sum of mass to charge ratios of 80, 81, 96, 97, 99, 177, 195, 197, and 293, of which the most abundant was 97 (HSO_4^-). Mass to charge ratios of 12, 13, 24, 25, 26, 27, 42, 43, 45, and 89 were used as a set of common organic peaks, of which the most abundant was 26 (CN^- and $C_2H_2^-$).

Figure 3. Several common types of positive ion spectra in the stratosphere. The most common type contained iron, magnesium, and other metals as well as sulfate (a). Positive ion spectra of sulfate particles without any metals were also observed (b). Some organic material and NO^+ was almost always present. Finally, some particles contained mercury (c), usually with a distinctive pattern of other peaks including a large C^+ peak and a peak at $m/z = 127$ that is presumed to be I^+. These spectra were obtained within minutes of each other at the same altitude, indicating a diverse mixture of aerosols in the stratosphere. The inset in (c) shows an expanded plot of the data along with the natural isotopes of Hg convoluted with the resolution of the mass spectrometer.

Figure 4. Frequency of iron in positive ion spectra. The leftmost bin contains spectra with no signal for iron. A mass to charge ratio of 56 was nearly unique for iron, as could be verified with $^{54}Fe^+$. Stratospheric data were defined as those at potential temperatures greater than 410 K and tropospheric as potential temperatures less than 380 K and at least 600 m below the tropopause measured by the MTP. Aerosols that contain iron were more frequent in the stratosphere than in the upper troposphere. The frequency of iron in the stratosphere was nearly constant with latitude, although there were slightly fewer iron containing spectra in the tropics than at mid-latitudes. There were insufficient data in the troposphere to separate the histograms by latitude.

Figure 5. The $^{39}K/^{23}Na$ ratio observed in aerosol particles which also contained iron for two different altitude ranges. Most of the spectra in the leftmost bin, which includes zero, did not have sufficient signal to noise to expect to see a small ^{39}K peak. Other symbols show $^{39}K/^{23}Na$ ratios measured for meteoritic and surface sources (15, 48, 49).

Figure 6. The vertical profile of the percentage of mercury ions as derived from ^{202}Hg, the most abundant isotope. This peak is nearly unique for mercury in the spectra of aerosol particles. Altitudes are referenced to the tropopause altitude determined by the microwave temperature profiles. Data from 25° N to 28°N are excluded because of frequent double or ambiguous tropopauses.

Figure 7. Examples of unusual particles. The inset in (b) shows an expanded plot of the data along with the natural isotopes of Ba convoluted with the resolution of the mass spectrometer.

Figure 8. Elements observed in aerosol particles at altitudes above 5 km. Frequencies are very approximate because of differing ionization efficiencies. Elements with a distinctive signature of isotopes are also more likely to be unambiguously observed than those with only one isotope. Certain elements are likely to be undercounted because of spectral interferences. For example, the main isotopes of Si and Ti can be obscured by CO and SO, respectively.

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Figure 1

Top panel — Stratosphere:

19980507 #6672
Stratosphere
19 km; 31°N
θ=437 K

Labeled peaks: O^-, OH^-, S^-, SO_3^-, HSO_3^-, SO_4^-, HSO_4^-, $H^{34}SO_4^-$

Detector Signal (mA) vs Ion mass/charge

Bottom panel — Troposphere:

19980501 #1120
Troposphere
14.6 km; 22°N
θ=360 K

Labeled peaks: H^-, O^-, OH^-, C_2^-, CN^- & $C_2H_2^-$, $^{35}Cl^-$, $C_2H_2O^-$, CHO_2^-, $CH_3CO_2^-$, $C_2H_5CO_2^-$, $^{79}Br^-$, SO_3^-, HSO_3^-, SO_4^-, HSO_4^-, $H^{34}SO_4^-$, $CH_2OHSO_3^-$, I^-

Detector Signal (mA) vs Ion mass/charge

(a)

Potential Temperature (K)

Legend:
- ···⊙··· < 25° N
- —⊟— > 31° N
- Means of ~260 spectra
- **Negative Ions**

Typical tropopause < 25°N

Typical tropopause > 31°N

Sulfate Peaks (fraction of total)

(b)

Potential Temperature (K)

Legend:
- ···⊙··· < 25° N
- —⊟— > 31° N
- Means of ~260 spectra
- **Negative Ions**

Subset of Organic Ions (fraction of total)

(a) 19980507 #6526 STRATOSPHERE 19 km; 32°N θ=439 K

$^{56}Fe^+$
NO^+
$^{24}Mg^+$
H_3O^+ Al^+
Na^+
S^+
SO^+
$^{40}Ca^+$
$^{54}Fe^+$
$FeOH^+$
$H_3SO_4^+$
$^{58}Ni^+$
HSO_3^+

(b) 19980507 #6550 STRATOSPHERE 19 km; 32°N θ=440 K

C^+
NO^+
$CO^+?$
S^+
SO^+
H_3O^+
SO_2^+ HSO_2^+
HSO_3^+
$H_3SO_4^+$

(c) #6789 19 km; 31°N θ=438 K

C^+
$CO^+?$
NO^+
H_3O^+
44^+
45^+: organic
I^+
Hg^+
Hg isotopic pattern
data

Figure showing "Fraction of spectra" versus $^{56}Fe^+$ (fraction of positive ions), with legend: Stratosphere > 31°N (dashed), Stratosphere < 25°N (dotted), Troposphere (solid).

Figure 5

K/Na ratio measured at 91-108 km after Perseids

Asian dust at Mauna Loa

road dust

Single Particle Data
- - - 17 to 19 km
—— 5 to 12.5 km

Fraction of Spectra

^{39}K / ^{23}Na in spectra containing Fe

(a) Positive Ions
19980506
#3137
18 km 45°N
(Stratosphere)

(b) Positive Ions
19980501
#2678
14.6 km 16°N
(Troposphere)

most many common some rare maybe

He

H

Li Be B C N O F Ne

Na Mg Al Si P S Cl Ar

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe

Cs Ba * Hf Ta W Re Os Ir Pt Au Tl Pb Bi Po At Rn

Fr Ra *

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Ac Th Pa U